

## TEMPERATURE-PROGRAMMED CATALYTIC LIQUEFACTION OF LOW RANK COAL USING DISPERSED Mo CATALYST

Lili Huang, Chunshan Song and Harold H. Schobert  
Fuel Science Program  
Department of Material Science and Engineering  
The Pennsylvania State University  
University Park, PA 16802

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### INTRODUCTION

In the presence of catalyst, the specific reaction conditions have a direct effect on conversion in coal liquefaction and on the product distribution [1]. At temperatures lower than 300°C, catalyst precursors such as ammonium tetrathiomolybdate may not be converted to a catalytically active form and thus have no benefit on liquefaction [2]. However, at severe reaction conditions, such as high temperature, retrogressive reactions will take place, and crosslinking or recombination of radicals generated in thermal cracking will reduce the possibility of breaking the coal macromolecule into smaller molecules. In an effort to achieve highest conversion and desired product distribution, low-severity processes have been studied by several research groups. It has been found that temperature-programmed and temperature-staged liquefaction are efficient to maximize the conversion and minimize the retrogressive reactions [3, 4, 5].

The objective of the work reported in this paper is to study the catalytic effect of ammonium tetrathiomolybdate, techniques to disperse this catalyst precursor onto coal, and the optimum reaction conditions for the highest conversion.

### EXPERIMENTAL

The coal sample was a Montana subbituminous (DECS-9, PSOC-1546) coal obtained from Penn State Coal Sample Bank. Its composition is summarized as follows: 24.68% moisture, 4.80% ash, 33.46% volatile matter and 37.06% fixed carbon on an as-received basis, 76.11% carbon, 5.14% hydrogen, 0.91% nitrogen, 0.33% organic sulfur and 17.50% oxygen on a dmmf basis. The coal was dried at 95°C in vacuum for two hours before use.

The catalyst precursor, ammonium tetrathiomolybdate (ATTM), was dispersed on coal by incipient wetness method. The loading was 1% of molybdenum on the basis of dmmf coal. Water and a mixture of H<sub>2</sub>O/THF (44 : 56) were employed as impregnation solvents. After loading of the catalyst precursor, the coal sample was dried in vacuum for two hours at 105°C, then removed and stored under a nitrogen atmosphere.

Liquefaction experiments were conducted in microautoclave reactors (tubing bombs) in a preheated fluidized sandbath. For each reaction, 4 grams of coal and 4 grams of Wilsonville Middle Distillate (WIMD) as reaction solvent were added to the reactor, following which hydrogen was purged three times, with a final pressure of 7 MPa at room temperature. The reactor was then plunged into the sandbath and agitated at 200 cycles per minute. The tubing bomb reached the reaction temperature in about three minutes. For a single-staged liquefaction (SSL), the tubing bomb was rapidly heated-up to 400°C and held for 30 minutes followed by rapid quench. For a temperature-programmed liquefaction (TPL), the tubing bomb was rapidly heated-up to a relatively low temperature (200°C-300°C) and soaked in sandbath at that temperature for 15 minutes. The

temperature was then gradually increased to a higher temperature level (400°C-450°C) and held for 30 minutes, followed by rapid quench. The rate of temperature increase was 30°C/min to 8.30°C/min, depending on the difference between the lower temperature and the higher temperature. The heat-up period was about 30 minutes, and the total reaction time was about 75 minutes. Temperature-staged liquefaction (TSL) was a different procedure from TPL. A tubing bomb was rapidly heated-up to a low temperature (200°C-300°C), soaked at that temperature for 15 minutes, then it was immediately (without a heating period) transferred to another sandbath of a higher temperature (400°C) and held for 30 minutes followed by rapid quench. Since there was no heating period between two temperature stages, the total reaction time was about 45 minutes, which is different from TPL.

After the reaction, the gaseous product was vented into a gas sample bag and later analyzed by gas chromatography. The liquid and solid products and residue were washed into a tared ceramic thimble using hexane. Then the products were separated under a nitrogen atmosphere by Soxhlet-extraction using hexane, toluene and THF as solvents, the products being classified as oil, asphaltene and preasphaltene respectively. Solvents were removed by rotary evaporation and the products were dried in vacuum at 110°C for about 12 hours, except for the hexane solubles. The solid residue was washed first by acetone and then by pentane several times and dried in the same procedure as the reaction products. The asphaltene, preasphaltene and residue were then weighed, and conversion and product distributions were calculated based on dmmf coal.

## RESULTS AND DISCUSSION

The effects of TPL and SSL are compared in Table 1. In the absence of a catalyst, TPL total conversion is 6.4 percentage units higher than SSL. This is mainly due to the gains in asphaltene and preasphaltene yields, while the oil yield remains almost identical in both cases, about 30.2%. In the presence of ATTM as catalyst precursor, total conversion increases again in TPL by 6.6 percentage units, similar to those experiments without catalyst. It is noticed that, different from non-catalytic liquefaction, the oil yield increases drastically by 8.8 percentage units in TPL, while asphaltene decreases by 4.9 percentage units. This may suggest that TPL, with presence of the catalyst, promotes the further cracking or hydrogenation of asphaltene to oil, though the detailed mechanism is not yet clear.

Another comparison is liquefaction with and without catalyst. In SSL runs, total conversion increases 32.2 percentage units by employing ATTM as catalyst. This is mainly due to an oil yield increase (by 12.5 percentage units) and an asphaltene yield increase (by 16.4 percentage units), and to a lesser extent, to a preasphaltene yield increase (by 3.3 percentage units). In TPL runs, catalytic liquefaction achieves 32.4 percentage units higher than non-catalyst run in total conversion. Gas and oil yield increases are the predominant (by 21.2%) contribution to the increase in total conversion. Asphaltene and preasphaltene increase by lesser amounts, 6.7 and 4.4 percentage units respectively. This comparison presents that the addition of ATTM as catalyst efficiently improves both the total conversion of liquefaction and the selectivity of products to the more desirable oils.

As mentioned in previous section, in the procedure of sample preparation, both H<sub>2</sub>O and H<sub>2</sub>O/THF (44 : 56) were employed as impregnation solvents. The volume of the H<sub>2</sub>O/THF mixture required to achieve incipient wetness is about three times of that of pure water. It is apparent that the mixture has higher affinity toward the coal surface than water. This difference in affinity may lead to a different dispersion of the catalyst precursor on coal, which will subsequently result in a difference of catalyst performance. Table 1 provides the conversion data to compare the solvent effect on liquefaction. For SSL runs, samples prepared using H<sub>2</sub>O/THF appear a bit more active than samples prepared using H<sub>2</sub>O. For TPL runs, the difference is more pronounced. By using H<sub>2</sub>O/THF as impregnation solvent, total conversion increases by 10.4 percentage units, which is due to the increase of gas and oil yield (by 10.3 percentage units). The asphaltene and

preasphaltene yields are identical within experimental error. This set of data supports the assumption that by employing H<sub>2</sub>O/THF, better catalyst dispersion will be achieved, thus leading to a better catalyst performance.

Temperature-programmed liquefaction may be advantageous over temperature-staged liquefaction because TPL provides a heating period which could slowly generated radicals and allow hydrogenation to take place. Table 2 compares TPL with TSL. For 200/400 runs (the first number indicates the first stage temperature and the second number indicates the second stage temperature), the total conversion increases slightly (1.5 percentage units) in TPL with a remarkable increase in gas and oil yield (7.5 percentage units). In contrast, the asphaltene and preasphaltene yields decrease slightly. For 300/400 runs, the same phenomenon is observed, though in 300/400 runs, both TPL and TSL achieve higher total conversion and gas oil yield. It is apparent that TPL is more favorable to achieve high conversion and better product selectivity. Consistent with the previous observations, the asphaltene yield decreases in TPL experiments. This again reflects the fact TPL promotes the interconversion of asphaltene to oils [6].

Figure 1 shows the conversion as a function of the temperature in the first stage in TPL runs. The curve starts at room temperature, which is in fact the SSL run. The total conversion reaches a maximum at 200°C (91%) and starts to decrease as temperature increases, 86.6% at 250°C and 89.7% at 300°C. The oil yield changes in a very similar way as total conversion, 51.5% at 200°C, 46.8% at 250°C and 50.6% at 300°C. The low temperature stage is used to allow time for the reaction solvent to penetrate into the interior of coal particles [3]. If the temperature of this stage is too high, the reaction solvent may evaporate before penetration. In this case, less solvent will be in the interior of coal and this could result in reduced H-transfer to the coal radicals, which will consequently cause poor liquefaction results. The temperature of the first stage may also affect the activation of catalyst precursor, but how this will subsequently affect the liquefaction is still unknown.

The effect of changing temperature of the second stage in TPL is shown in Figure 2. Although the total conversion, as well as the yields of asphaltenes and preasphaltenes, show a trend of decreasing, the gas and oil yields show a remarkable increase as the temperature increase from 400°C to 450°C (51.5% to 62.4%). This indicates that an increase of second stage temperature may not favor high total conversion of liquefaction, but it has some benefit in achieving high yield of oil and gas. The decrease of total conversion might be caused by retrogressive reactions. At temperatures as high as 450°C, radicals formed in thermal cracking immediately crosslink and recombine with one another to form some very stable compounds that are difficult to liquefy.

## CONCLUSIONS

Addition of ATTM as catalyst precursor will increase the total conversion substantially. In the impregnation procedure, using organic compounds in the impregnation solvent appears to lead to a better dispersion of catalyst precursor thus giving a higher conversion. Temperature-programmed liquefaction is advantageous over temperature-staged and single-staged liquefaction regardless of whether a catalyst is used. The change of first and second stage temperature in TPL will influence the conversion, though determining the reasons for these influences relies on future research.

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Table 1. Comparison of TPL and SSL Effect on Liquefaction.

Sample	rxn Cond.	Tot Conv.	Gas + Oil	Asph.	Preasph.
Non-cat	SSL	52.22	30.21	12.46	9.55
	TPL	58.57	30.27	17.24	11.06
ATIM THF/H <sub>2</sub> O	SSL	84.4	42.73	28.86	12.82
	TPL	91	51.49	23.93	15.5
ATIM H <sub>2</sub> O	SSL	83.24	38.98	19.46	24.8
	TPL	80.57	41.18	23.4	15.42

Oil: hexane soluble.

Asphaltene: toluene soluble but hexane insoluble.

Preasphaltene: THF soluble but toluene insoluble

Table 2. Comparison of TPL with TSL.

Temperature	rxn Cond.	Tot. Conv.	Gas + Oil	Asph.	Preasph.
200/400	TPL	91	51.49	23.93	15.5
	TSL	89.46	43.98	27.62	17.87
300/400	TPL	89.67	50.61	22.67	16.4
	TSL	87.91	42.66	28.37	16.89

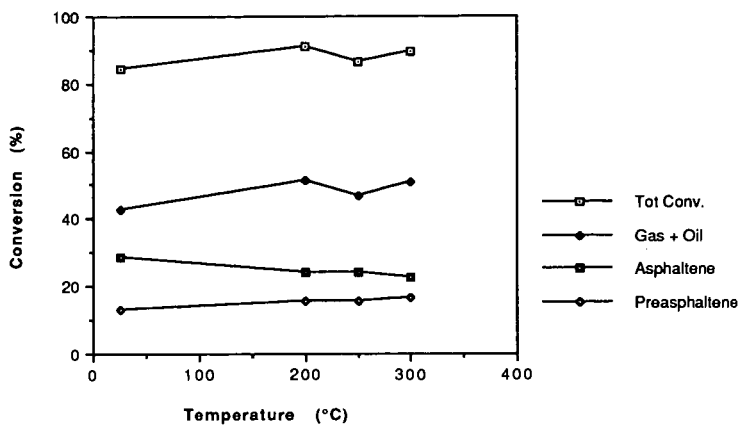


Figure 1. Conversion as a function of first stage temperature in TPL.

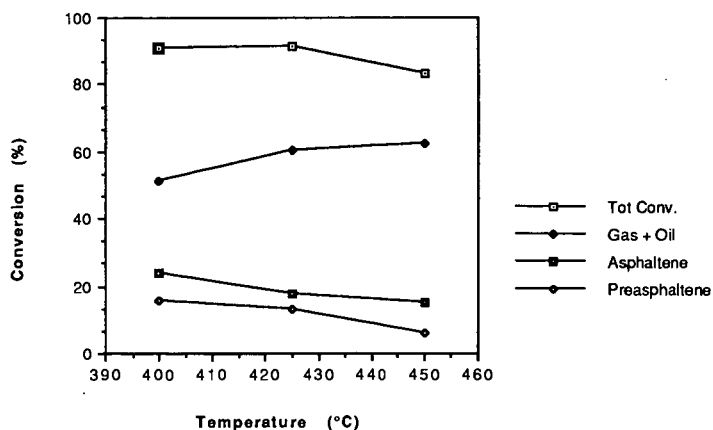


Figure 2. Conversion as a function of second stage temperature in TPL.